(19)【発行国】日本国特許庁（ＪＰ）

(12)【公報種別】公開特許公報（Ａ）

(11)【公開番号】特開平６－１８８０３０

(43)【公開日】平成６年（１９９４）７月８日

(54)【発明の名称】非水電解質電池

(51)【国際特許分類第５版】

H01M 10/40 Z

B

【審査請求】未請求

【請求項の数】４

【全頁数】３

(21)【出願番号】特願平４－３５５９４３

(22)【出願日】平成４年（１９９２）１２月１８日

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(19) [Publication Office] Japanese Patent Office (JP)

(12) [Kind of Document] Japan Unexamined Patent Publication (A)

(11) [Publication Number of Unexamined Application (A)] Japan Unexamined Patent Publication Hei 6 - 188030

(43) [Publication Date of Unexamined Application] 1994 (1994) July 8 day

(54) [Title of Invention] NONAQUEOUS ELECTROLYTE BATTERY

(51) [International Patent Classification 5th Edition]

H01M 10/40 Z

B

[Request for Examination] Examination not requested

[Number of Claims] 4

[Number of Pages in Document] 3

(21) [Application Number] Japan Patent Application Hei 4 - 355943

(22) [Application Date] 1992 (1992) December 18 day

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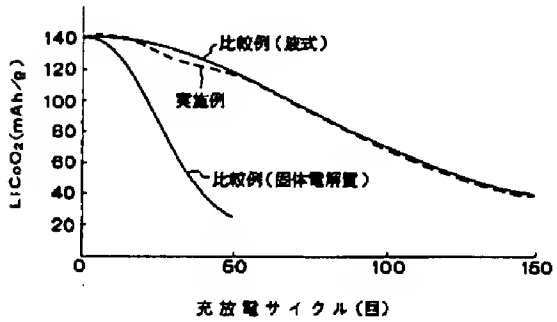
(57)【要約】

【目的】　有機固体電解質を含む非水電解質電池の充電放電サイクル特性、自己放電の低減、エネルギー効率の向上及び電池の安全性向上など電池の信頼性の向上を計ることを目的とする。

【構成】　有機固体電解質と、遊離した液状の電解液とを共存せしめた非水電解質電池とすることにより上記目的を達成できる。



【特許請求の範囲】

【請求項１】　有機固体電解質と、遊離した液状の電解液とを共存せしめたことを特徴とする非水電解質電池。

【請求項２】　前記有機固体電解質が、正極又は負極の表面を覆っていることを特徴とする請求項１記載の非水電解質電池。

【請求項３】　前記正極又は負極が、インターカレーションによりリチウムイオンの出し入れを行う物質であることを特徴とする請求項１又は２記載の非水電解質電池。

【請求項４】　前記負極の面積が、正極の面積より大きく且つ有機固体電解質で被覆されていることを特徴とする請求項１、２又は３記載の非水電解質電池。

【発明の詳細な説明】

[Name] Murata　Kazuo

(57) [Abstract]

[Objective] Charge-discharge cycle property of nonaqueous el ectrolyte battery which includes organic solid electrolyte, it designates thatimprovement of reliability of battery such as decrease of self discharging,improvement of energy efficiency and safety improvement of battery is assuredas object.

[Constitution] Above-mentioned objective can be achieved by making nonaqueous electrolyte battery whichcoexists with electrolyte solution of liquid which separates with organic solid electrolyte.

[Claim(s)]

[Claim 1] Nonaqueous electrolyte battery which designates tha t it coexists with electrolyte solution of theliquid which separates with organic solid electrolyte, as feature.

[Claim 2] Aforementioned organic solid electrolyte, nonaqueo us electrolyte battery which is stated in Claim 1 whichdesignates that surface of positive electrode or negative electrode has been covered as feature.

[Claim 3] Aforementioned positive electrode or negative elect rode, nonaqueous electrolyte battery which is stated in Claim 1 or 2 whichdesignates that it is a substance which takes in and out lithium ion withthe intercalation as feature.

[Claim 4] Surface area of aforementioned negative electrode, t o be larger than surface area ofthe positive electrode and nonaqueous electrolyte battery which is stated in Claim 1, 2 or 3 which designatesthat it is covered with organic solid electrolyte as feature.

[Description of the Invention]

【０００１】

【産業上の利用分野】本発明は、エレクトロニクス機器、電気自動車、玩具、アクセサリーなどの分野に使われる非水電解質電池に関するものである。

【０００２】

【従来の技術】従来の非水電解質電池としての液系と固体電解質系において、液系の電池では約５００サイクル程の充電放電サイクルが得られているが、エネルギー効率の点から固体電解質系の電池では１００～２００サイクル程度しか達成されていない。即ち充電放電サイクルと共に正極活物質及び負極活物質の利用率が低下すること、及び自己放電が大きいことによるものである。

【０００３】

【発明が解決しようとする課題】本発明は上記問題点に鑑みてなされたものであって、その目的とするところは有機固体電解質を含む非水電解質電池の充電放電サイクル特性、自己放電の低減、エネルギー効率の向上及び電池の安全性向上など電池の信頼性の向上を計るものである。

【０００４】

【課題を解決するための手段】本発明は上記目的を達成するもので、有機固体電解質を含み且つ遊離した液状の電解液とを共存せしめたこと、前記有機固体電解質が正極又は負極の表面を覆っていること、前記正極又は負極がインターカレーションによりリチウムイオンの出し入れを行う物質であること、及び前記負極の面積が正極の面積より大きく且つ有機固体電解質で被覆されていることなどにより問題点を解決することを特徴とするものである。

【０００５】

【作用】請求項１により電池の安全性を高めると共にイオン伝導性を高め、電池の性能信頼性を向上させる。即ち液系電解質の場合、負極活物質と正極活物質がセパレーターの微孔を通して直接接触し電池破損することが多く、固体電解質系では電解質が固体であるためイオンの伝導性が悪く抵抗が高くなり、高い電流が取り出せないなど安全性及び電池性能の点で問題がある。請求項２に

[0001]

[Field of Industrial Application] This invention is something regarding nonaqueous electrolyte battery which is used in electronics equipment ,the electric car , toy and accessory or other field.

[0002]

[Prior Art] With battery of liquid type charge-discharge cycle about of approximately 500 cycle isacquired in liquid system and solid electrolyte system as conventional nonaqueous electrolyte battery,, but with thebattery of solid electrolyte type only 100 to 200 cycle extent it is achieved from point ofthe energy efficiency. Namely with charge-discharge cycle use ratio of positive electrode active material and negative electrode active material decreases,it is something due to fact that and self discharging arelarge.

[0003]

[Problems to be Solved by the Invention] As for this invention considering to above-mentioned problem, beingsomething which you can do, purpose charge-discharge cycle property of nonaqueous electrolyte battery whichincludes organic solid electrolyte, is something which assures improvement of thereliability of battery such as decrease of self discharging, improvement of the energy efficiency and safety improvement of battery.

[0004]

[Means to Solve the Problems] As for this invention something which achieves above-mentioned objectbeing, organic solid electrolyte implication and it coexisted with electrolyte solution of liquidwhich separates, Aforementioned organic solid electrolyte has been covered surface of positive electrode or negative electrode, theaforementioned positive electrode or negative electrode it is a substance which takes in and out lithium ionwith intercalation , it is something which designates that problem issolved with etc being covered with organic solid electrolyte and surface areaof aforementioned negative electrode to be larger than surface area of positive electrodeand as feature.

[0005]

[Work or Operations of the Invention] As safety of battery is raised with Claim 1 it raises theionic conductivity, performance reliability of battery improves. Namely in case of liquid electrolyte, negative electrode active material and positive electrode active material direct contactit does through micropore of separator and it becomes many times whenthe battery breakage it does, because with solid electrolyte system

より有機固体電解質を正極又は負極の表面を被覆することで、接触性を高めイオンの伝導性をよくする。また固体電解質が正極と負極の間隙を自由に動けないため内部短絡が防止され、安全性も高まる。また電池製作時に正極又は負極の表面に有機固体電解質を塗工することで、取扱い性が高まり厚さの制御も容易となる。さらに電池の組み立ても容易となる。請求項３により正極又は負極物質をリチウムのインターカレーション物質とすることで上記した安全性と、充電時の内部短絡を防止できる。さらに正極及び又は負極の活物質の利用率が従来に比べて高まった。これはリチウムイオンの移動ロスが少ないことによるもので電解質を固体と液体の共存系としたことに起因している。また電池を量産する場合の極板作製が印刷方式を採用でき、任意の形状の電池を生産できる。請求項４により負極面積を正極面積より大きくすることで、負極端部での電流集中によるリチウムの偏析が防止され電池内部短絡による寿命低下を防止する。また有機固体電解質を負極面に被覆することにより負極物質と有機固体電解質との接触が良くなりリチウムイオンの移動が良好となると共に偏析が防止でき電池の利用率及び安全性が向上する。

electrolyte is solid,the conductivity of ion to be bad resistance high, such as cannot removethe high current there is a problem in point of safety and thebattery performance. organic solid electrolyte by fact that surface of positive electrode or negative electrode is covered, the contact property is raised and with Claim2 conductivity of ion is improved. In addition solid electrolyte gap of positive electrode and negative electrode because it cannot movefreely, internal short circuit is prevented, also safety increases. In addition by fact that at time of battery manufacturing organic solid electrolyte ispainted in surface of positive electrode or negative electrode, handling property increases and alsocontrol of thickness becomes easy. Furthermore also assembly of battery becomes easy. internal short circuit at time of safety and charge which were inscribedby fact that positive electrode or negative electrode substance is designated as intercalation substance of lithiumwith Claim3 can be prevented. Furthermore use ratio of active substance of positive electrode and/or negative electrode it increased incomparison with past. This being something due to fact that portable loss of lithium ionis little electrolyte has originated in making copresent system of solidand liquid. In addition pole plate preparation when mass production it does battery be able toadopt printing system, battery of optional shape can be produced. By fact that it enlarges than positive electrode surface product, segregation of thelithium due to current concentration with negative electrode end is prevented negative electrode surface product bythe Claim4 and prevents lifetime decrease with battery internal short circuit. In addition as contact with negative electrode substance and organic solid electrolyte becomes good andby covering organic solid electrolyte in negative electrode surface movement of lithium ion becomessatisfactory, it can prevent segregation and use ratio and safety ofthe battery improve.

【０００６】

【実施例】以下、本発明の実施例を説明する。リチウムインターカレーション能力をもつカーボン微粉末をＰＶｄＦ（ポリフッ化ビニリデン）のＮ－メチルピロリドン溶液に分散させ、帯状銅箔に塗布し、Ｎ－メチルピロリドンを揮発させカーボン負極を作製した。またＬｉＣｏO_2微粉末とアセチレンブラックを１０：１の重量比で混合しておき、ゴム系樹脂（ＥＰＤＭ）のトルエン溶液に分散させ、帯状アルミニウム箔に塗布し、トルエンを揮発させＬｉＣｏO_2正極を作製した。さらにγ－ブチルラクトンに１モル／ｌのＬｉＢF_4を溶解させた電解液と重量平均分子量１，０００のポリエチレンオキシドジアクリレートを約３：１の重量比で混合し、ガラス微粉を分散させ、ペースト状とした。次に該ペーストを上記負極上に塗布し、電子線を照射してペーストを硬化させ固体電解質とした。上記正極及び固体電解質／負極合体を重ね合わせて巻き込み、集電体を兼ねる円筒状（又は角形）電池容器内に挿入した。次にγ－ブチルラクト

[0006]

[Working Example(s)] Below, Working Example of this invention is explained. Dispersing carbon fine powder which has lithium intercalation capacity to N-methyl-pyrrolidone solution of PVdF (polyvinylidene fluoride), itapplied to strip copper foil, volatilization did N-methyl-pyrrolidone and produced carbon negative electrode. In addition it mixed LiCoO2 fine powder and acetylene black with weight ratio of the10:1, dispersed to toluene solution of rubber type resin (EPDM), applied to strip aluminum foil, thevolatilization did toluene and produced LiCoO2 positive electrode. Furthermore it mixed polyethylene oxide diacrylate of electrolyte solution and weight average molecular weight 1,000 which meltthe LiBF4 of 1 mole/liter in -butyl lactone with weight ratio of approximately3:1, dispersed glass fine powder, made paste. Applying said paste next on above-mentioned negative electrode, irradiating the electron beam and hardening paste it made solid electrolyte. Superposing above-mentioned positive electrode and solid

ンに１モル／ｌのＬｉＢＦ$_4$を溶解させた電解液を上記電池容器内に一定量注液（例えば真空含浸などの方法による。）した後、開口部を封口しＡＡサイズの非水電解質電池を作製した。なお電解液を過剰に注液した場合は含浸後に電解液を取り除いてもよい。

electrolyte / negative electrode engaged body, it inserted intothe cylinder (or square) battery container which combines entraining and current collector. electrolyte solution which melts LiBF4 of l mole/liter in - butyl lactone next theconstant amount pouring liquid after (It depends on for example vacuum impregnation or other method), opening was sealed inside above-mentioned battery containerand nonaqueous electrolyte battery of AA size was produced. Furthermore when pouring liquid it does electrolyte solution in excess,after impregnating it is possible to remove electrolyte solution.

【０００７】このような非水電解質電池を、電極の作用面積に対して１．５ｍＡ／ｃｍ^2、４．１Ｖの定電流定電圧充電及び０．５ｍＡ／ｃｍ^2、２．７Ｖの定電流放電を繰り返す充電放電サイクル試験を行った。

[0007] Constant current constant voltage charging of 1.5 mA/ cm2 and 4.1V and charge-discharge cycle test which repeats theconstant current discharge of 0.5 mA/cm2 and 2.7V were done this kind of nonaqueous electrolyte battery,vis-a-vis acting surface area of electrode.

【０００８】発明による電池性能比較を行うため、以下に比較電池の構成を説明する。正極及び固体電解質／負極合体を上記実施例と同様に作製し、且つそれらを重ね合わせて巻き込み、集電体を兼ねる円筒状（又は角形）電池容器内に挿入し、開口部を封口して比較例による電池を製した。この場合、本発明電池との違いは電池容器内に装填した後の電解液の補填がないことである。

[0008] In order to do battery performance comparison due to i nvention, constitution of comparison batteryis explained below . It produced positive electrode and solid electrolyte / negative electrode closure in same way as theabove-mentioned Working Example, and superposed those and it insertedinto cylinder (or square) battery container which combines entraining and current collector, sealedthe opening and make it did battery due to Comparative Example. In this case, difference with this invention battery loading after doing, isnot to be compensation of electrolyte solution inside battery container.

【０００９】さらに他の比較電池の構成を説明する。負極及び正極を前記した実施例と同様に作製した。次に該負極と正極の間にＰＰ微多孔膜を挟み、それらを巻き込み集電体を兼ねる円筒状（又は角形）電池容器内に挿入した後、実施例と同様の電解液に界面活性剤を添加した電解液を一定量注液し電池を作製した。

[0009] Furthermore constitution of other comparison battery is explained. Were produced in same way as Working Example which negative electrode and thepositive electrode before was inscribed. Putting between PP microporous membrane between said negative electrode and positive electrode next, thoseafter inserting into cylinder (or square) battery container which combines entraining current collector, theconstant amount pouring liquid it did electrolyte solution which adds surfactant to electrolyte solution which issimilar to Working Example and produced battery.

【００１０】これらの電池の充放電サイクルに対するエネルギー効率の変化を図１に示す。即ち、本発明の電池は従来の液系電解質にほぼ近いサイクル性能を示している。また固体電解質のみの系に対しては約３．１倍の性能向上となった。

[0010] Change of energy efficiency for charge-discharge cycle of these battery is shown in theFigure 1. Namely, battery of this invention has shown cycle performance which is almostclose to conventional liquid electrolyte. In addition vis-a-vis system only of solid electrolyte it became performance improvementof approximately 3. 1 times.

【００１１】

[0011]

【発明の効果】上述したことから本発明は次に記載する効果を奏する。

[Effects of the Invention] This invention has effect which is sta ted next from fact that thedescription above it does.

（１）エネルギー効率が液系の電池とほぼ同等になった

(1) Energy efficiency almost became equal to battery of liquid t

（２）液系の電池に比べ安全性が高い。

（３）固体電解質だけのものに比べ充放電サイクル性能が向上した。

（４）電池生産性が向上した。

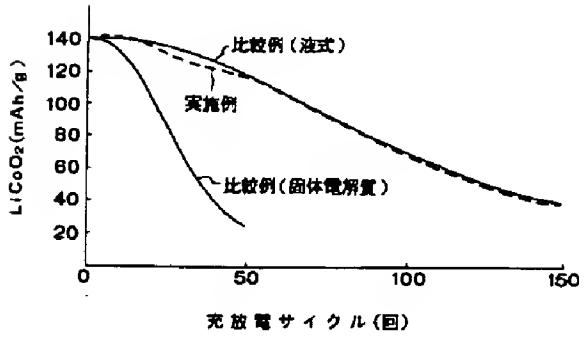
（５）内部短絡による電池破損が少なくなった。

（６）自動化が可能となった。

なお本発明においては円筒状の電池についての性能比較を行っているが、当然電池形状には限定されるものではなく、角型電池、シート状電池などに適用できる。なお正極及び負極の厚さ及び量、固体電解質及び電解液との厚さ及び量などの関係は電池サイズにより最適値が決定されるもので、特に限定するものではない。

【図面の簡単な説明】

【図１】本発明に係わる実施例と比較例による電池の充放電サイクルに対するエネルギー効率の変化を比較する特性図である。



【図１】

ype.

(2) Safety is high in comparison with battery of liquid type.

(3) Charge-discharge cycle performance improved in compariso n with those just of solid electrolyte .

(4) Battery production characteristic improved.

(5) Battery breakage due to internal short circuit decreased.

(6) Automation became possible.

Furthermore regarding to this invention, it does performance co mparison concerning thebattery of cylinder, but it is not something which is limited naturallyin battery shape , it can apply to rectangular battery and sheet battery etc. Furthermore thickness of thickness or quantity, the solid electrolyte or electrolyte solution of positive electrode and negative electrode or relationship of quantitativeor other being something where optimum value is decided by battery size , are notsomething which especially it limits.

[Brief Explanation of the Drawing(s)]

[Figure 1] It is a characteristic graph which compares change of energy efficiency for charge-discharge cycle ofthe battery due to Working Example and Comparative Example which relate to this invention.

[Figure 1]